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(21) International Application Number: PCT/US93/06289 (22) International Filing Date: 1 July 1993 (01.07.93) (30) Priority data: 07/911,239 9 July 1992 (09.07.92) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventor: DIESEN, Ronald, W. ; 5802 Flaxmoor Street, Midland, MI 48640 (US). (74) Agent: O'KEEFE, Robert, M.; The Dow Chemical Com- pany, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AU, BR, CA, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: DEHYDROCYCLIZATION OF UNSATURATED HYDROCARBONS TO AROMATIC PRODUCTS (57) Abstract Aromatic compounds such as ethylbenzene and styrene are produced by contacting butadiene or 4-vinylcyclohexene in a flow reactor with a magnesium oxide, zinc oxide, calcium oxide, strontium oxide, or barium oxide. The products of the process contain low levels of xylene.		

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DEHYDROCYCLIZATION OF UNSATURATED HYDROCARBONS TO AROMATIC PRODUCTS

Background of the Invention

5 The present invention relates to methods for converting butadiene to aromatic compounds.

 Ethylbenzene is an important commercial solvent and a precursor to styrene. Styrene is a major commercial chemical which finds its principal use in the manufacture of polymers such as polystyrene. Typically, styrene is formed by the dehydrogenation of
10 ethylbenzene. Both ethylbenzene and styrene may be produced by catalytic dehydrocyclization of 4-vinylcyclohexene ("VCH") by use of various known catalysts. Two-step processes for producing styrene and ethylbenzene are also known wherein butadiene is dimerized to form VCH and the VCH is then catalytically aromatized.

 However, the prior art lacks methods of producing styrene and ethylbenzene
15 directly from butadiene. Methods for the aromatization of VCH, moreover, have been plagued with poor yields and large amounts of by-products such as xylene which are extremely difficult to separate from the desired products.

 For example, Suzuka et al. sealed magnesium oxide and butadiene in a quartz reactor at 200°C for 17 hours to produce ethylbenzene in a yield of about 17 percent. Applied
20 Catalysis, Vol. 47, L7-L8 (1989). However, the major product of the reaction was o-xylene in a yield of about 54 percent.

 What is needed are new, more selective and effective processes for the production of aromatics such as ethylbenzene and styrene which alleviate problems in the prior art. What is also needed is a process to produce aromatics directly from butadiene thereby
25 offering a new method of producing the aromatics in one step.

Summary of Invention

 This invention, in one respect, is a process to produce ethylbenzene or styrene or mixtures thereof which comprises contacting a moving feedstream containing butadiene or 4-vinylcyclohexene or both with a catalyst in the gas phase under conditions effective to
30 convert at least a portion of the butadiene or 4-vinylcyclohexene or both to ethylbenzene or styrene or mixtures thereof, wherein the catalyst is selected from the group consisting of magnesium oxide, zinc oxide, calcium oxide, strontium oxide, and barium oxide, and wherein the products contain less than 5 mole percent of xylene.

 Thus, it has been found that butadiene can be converted to aromatic products
35 such as ethylbenzene and styrene by catalytic aromatization in the presence of certain catalysts. The products formed therefrom have low amounts of by-products and are produced in high yield and high selectivity. The catalysts found effective in these processes include magnesium oxide and zinc oxide.

Detailed Description of Illustrative Embodiment

Suitable catalysts of this invention include metal oxides such as magnesium oxide, zinc oxide, calcium oxide, strontium oxide, and barium oxide. The metal oxides can be employed in a variety of physical shapes such as pellets, granules, and spheroids. The metal
5 oxides can be bound with conventional binders such as alumina and silica. In a transport reactor, it is preferred to use a spherically shaped metal oxide. Prior to use, the metal oxide can be calcined using conventional techniques. Preferred metal oxides are magnesium oxide and zinc oxide. Most preferably, the metal oxide is magnesium oxide.

When desired, the catalysts of the present invention can be regenerated by
10 techniques known to those skilled in the art. For example, the catalysts can be regenerated by passing an oxygen-containing gas over the catalyst at elevated temperatures.

The feedstream to be converted in accordance with this invention contains butadiene or VCH or both. The butadiene and VCH need not be 100 percent pure and can contain other hydrocarbons such as alkanes, alkenes, cyclic aliphatics, and aromatics. Thus, this
15 invention is useful for converting butadiene which is found in product streams of crackers, for example, which are utilized widely in industry. The feedstream of this invention can also comprise inert carrier gases such as nitrogen, helium, argon, carbon dioxide, and steam. The feedstream is substantially free of gaseous oxygen with no greater than 1 percent by volume of the feedstream being gaseous oxygen. A feedstream useful in this invention contains greater
20 than 10 percent by volume of butadiene or VCH or both. Preferably, the feedstream contains greater than 20 percent by volume of butadiene or VCH or both.

The process of the present invention is carried out in the gas phase at a temperature in the range from 400°C to 625°C. Preferably, the temperature is from 450°C to 600°C. The pressure can be subatmospheric, atmospheric, or superatmospheric. Preferably the
25 pressure is superatmospheric. When pressure is superatmospheric, it is preferred that pressure be less than 25 atmospheres, more preferably less than 10 atmospheres.

The processes of the present invention can be carried out in the gas phase in a variety of flow reactors. Examples of suitable reactors include batch reactors, continuous fixed-bed reactors, fluidized bed reactors, and moving bed reactors. Preferably, the reactor is a
30 continuous flow reactor such as a fixed-bed reactor or is a moving bed reactor such as a falling solids reactor or a riser reactor. The flow rate of feedstream in a continuous flow reactor is expressed as the gas hourly space velocity (GHSV) and is given in units of volume of gaseous feedstream per total reactor volume per hour or simply hr^{-1} . The reactor can be operated with a flow rate of reactant in the range from 100 hr^{-1} to $36,000 \text{ hr}^{-1}$. A more preferred commercial
35 reactor for the process of this invention is a moving bed reactor, such as a riser reactor.

Typically, a riser reactor comprises an upright vessel of relatively low ratio of diameter to length. The catalyst is continuously charged into the bottom of the riser reactor. Likewise, the butadiene feedstream is delivered concurrently to the bottom of the riser reactor

as a vapor phase feed or as a liquid phase feed. Preferably, the butadiene feedstream is delivered as a vapor phase feed. The butadiene feedstream moves upward through the reactor, thereby contacting the catalyst. The feedstream and catalyst rise through the reactor and the butadiene is transformed in a single pass to form products of the process. The catalyst is typically separated from the feedstream and products of the process by use of a stripping gas which is delivered to the reactor after the feedstream and catalyst have contacted to produce products. Any conventional stripping gas can be used for this purpose, but VCH is preferred. The product stream exits the riser reactor and is separated by known methods, such as distillation, condensation, adsorption, and zone freezing, to recover the desired products. Unreacted butadiene can be recycled to the riser reactor for further conversion.

The operation of a riser reactor can be simulated by employing a method of alternating pulses of butadiene diluted by an inert gas through a fixed catalyst bed such that the volume ratio of butadiene to catalyst is high. Thus, a pulse of a butadiene feedstream is passed through the catalyst bed wherein the butadiene is converted to products. Next, a pulse of stripper gas is passed through the catalyst bed to purge the bed of residual hydrocarbons. When required, the catalyst can be regenerated by passing an oxygen-containing gas over the catalyst at elevated temperatures. Likewise, in a riser reactor, it is preferred to maintain a high ratio of gas volume to catalyst volume. In other words, a low catalyst loading should be employed in a riser reactor.

When the process of this invention is conducted in a moving bed reactor, described hereinbefore, the flow rate of the reactants can be varied. Generally, in the process of this invention the butadiene feedstream is fed into the reactor at any operable flow rate which promotes the formation of products and yields the desired conversion and selectivity. Preferably, the flow rate of the feedstream in the moving bed reactor is 100 hr^{-1} to $20,000 \text{ hr}^{-1}$. It should be understood that the space velocity controls the residence time of the reactants. Residence times suitable in the practice of this invention are from one-half second to 10 seconds, preferably from 1 to 10 seconds. Desirable residence times are inversely related to pressure. Thus, as pressure in the reactor is increased, the more preferable residence time is lowered. The most desirable residence times are readily determined by a skilled artisan depending on the pressure in the reactor as well as other process conditions.

The process of the present invention converts butadiene feedstream to ethylbenzene and styrene with no greater than 5 weight percent of the products being xylene. Preferably, the amount of xylene in the product is less than 4, more preferably less than 3. In addition to ethylbenzene and styrene, the product stream can contain other aromatics such as benzene and toluene as well as by-products of various types. For example, small quantities of

cracking products, such as propylene and ethylene, can be formed. The amount of by-products formed is typically low.

For the purposes of this invention, "conversion" is defined as the mole percentage of butadiene or VCH lost from the feedstream as a result of reaction. The conversion can vary widely depending upon the reactants, the form of the catalyst, and the process conditions such as temperature, pressure, flow rate, and catalyst residence time. Within the preferred temperature range, as the temperature increases the conversion generally increases. Within the preferred gas hourly space velocity range, as the space velocity increases the conversion generally decreases. Typically, the conversion of butadiene or VCH is at least 10 mole percent. Preferably, the conversion is at least 20 mole percent; more preferably, at least 30 mole percent; even more preferably, at least 40 mole percent; and most preferably, at least 50 mole percent.

Likewise, for the purposes of this invention "selectivity" is defined as the mole percentage of converted butadiene which forms ethylbenzene or styrene or both. Generally, selectivities also vary widely depending upon the reactants, the form of the catalyst, and the process conditions. Typically, the process of this invention achieves high selectivities to ethylbenzene or styrene or both. Within the preferred temperature range, as the temperature increases the selectivity generally decreases. Within the preferred space velocity range, as the space velocity increases the selectivity generally increases. Typically, the selectivity to ethylbenzene or styrene or both is at least 40 mole percent. Preferably, the selectivity to ethylbenzene or styrene or both is at least 50 mole percent, more preferably at least 60 mole percent, most preferably at least 70 mole percent.

The concept of simultaneous high conversion and high selectivity can be conveniently expressed in terms of yield. For the purposes of this invention, the term "yield" refers to the numerical product of the single-pass conversion and selectivity. For example, a process according to the present invention operating at a conversion of 0.65, or 65 mole percent, and a selectivity of 0.75, or 75 mole percent, would have a yield of 0.49, or 49 mole percent. Typically, the yield achieved in the process of this invention is at least 8 mole percent. Preferably, the yield achieved in the process of this invention is at least 18 mole percent, more preferably at least 28 mole percent, most preferably at least 35 mole percent.

Subsequent to aromatization of at least a portion of the feedstream, the aromatized products can be separated and recovered by conventional techniques. The products and remainder of the feedstream are, for instance, continuously separated from the catalyst in a fixed bed reactor by gas movement through the catalyst bed. In the case of a riser reactor, the separation is accomplished by a stripping gas such as VCH charged counter current

to the falling catalyst. For example, the product can be condensed to form a liquid and residual butadiene can be removed by vacuum or distillation. Recovered butadiene can be recycled to the reactor, thus facilitating very high conversions of unsaturated hydrocarbons of up to 100 percent.

5 The following examples are given to illustrate the invention and should not be construed as limiting its scope. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

10 Conversion of Butadiene to Ethylbenzene Using Magnesium Oxide

A 1/2 inch cylindrical steel reactor having a concentric 1/8 inch thermocouple well was filled with 3.9 grams of MgO chips as a catalyst. The reactor was placed in an aluminum
15 block heater with a temperature controller. The reactor void space in the heated zone was 8 cubic centimeters. The feed composition and the products of reaction are measured with an on-line gas chromatograph through heated sample lines. The MgO chips were made from compressed wafers. The surface area of the MgO catalyst was 180 square meters per gram. For a feedstream of 38 mole percent butadiene in nitrogen, 15 psig, and a gas hourly space velocity
20 of 190 hr⁻¹, a conversion of 18 percent was observed at 450°C. The selectivity to ethylbenzene was 70 percent with benzene and VCH being major by-products. Yield of ethylbenzene was 12.6 percent. Butenes were formed as minor products. No styrene was observed under these conditions.

25 EXAMPLE 2

Conversion of Butadiene to Aromatics Using Magnesium Oxide

The procedure of Example 1 was repeated in a similar quartz reactor except that
30 the temperature was 560°C, the gas hourly space velocity was 1500 hr⁻¹ in a one minute pulse, and 2 grams of MgO was used and the feedstream was a pulsed feedstream comprising 21 mole percent butadiene in nitrogen. Conversion of 19 percent was achieved. Selectivities were as follows: ethylbenzene, 48 mole percent; styrene, 12 mole percent; butene, 12 mole percent; benzene, 6 mole percent; VCH, 6 mole percent; toluene, 5 mole percent; and unknowns, 11
35 mole percent. The total yield of styrene and ethylbenzene was 11 mole percent.

EXAMPLE 3

Conversion of Butadiene to Styrene and EthylbenzeneUsing Zinc Oxide

5 The procedure of Example 1 was repeated except zinc oxide was the catalyst in an amount of 3.5 grams. The gas hourly space velocity was 120 hr⁻¹. At 450°C the butadiene conversion was 20 percent. Selectivities were as follows: ethylbenzene, 60 mole percent; styrene, 10 mole percent; butene, 24 mole percent; benzene, 2 mole percent; and VCH, 3 mole percent. The yield of ethylbenzene and styrene was 14 percent. The activity of ZnO decreases
10 more quickly as compared to the MgO catalyst.

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CLAIMS

1. A process to produce ethylbenzene or styrene or mixtures thereof which comprises contacting a moving feedstream containing butadiene or 4-vinylcyclohexene or both with a catalyst in the gas phase under conditions effective to convert at least a portion of the butadiene or 4-vinylcyclohexene or both to ethylbenzene or styrene or mixtures thereof, wherein the catalyst is selected from the group consisting of magnesium oxide, zinc oxide, calcium oxide, strontium oxide, and barium oxide, and wherein the products contain less than 5 mole percent of xylene.
2. The process of Claim 1 wherein the flow rate of the moving butadiene feedstream has a gas hourly space velocity of from 100 to 36,000 hr⁻¹.
3. The process of Claim 1 wherein the temperature is from 450°C to 600°C.
4. The process of Claim 1 wherein the catalyst is magnesium oxide.
5. The process of Claim 1 wherein the process is conducted in a fixed bed reactor or a moving bed reactor.
6. The process of Claim 1 wherein the selectivity to ethylbenzene or styrene or both is at least 50 mole percent.
7. The process of Claim 1 wherein the catalyst is magnesium oxide or zinc oxide.
8. The process of Claim 1 wherein the products contain less than 3 mole percent of xylene.
9. The process of Claim 1 wherein the pressure is superatmospheric.
10. The process of Claim 8 wherein the pressure is less than 10 atmospheres.
11. The process of Claim 1 wherein residence time of the butadiene is from 1 second to 10 seconds.

INTERNATIONAL SEARCH REPORT

PCT/US 93/06289

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C07C15/073; C07C15/46; C07C2/76; C07C5/367																	
II. FIELDS SEARCHED <div style="text-align: center; border: 1px solid black; padding: 2px;">Minimum Documentation Searched⁷</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 20%; padding: 5px;">Classification System</td> <td style="padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">Int.Cl. 5</td> <td style="padding: 5px;">C07C</td> </tr> </table> <div style="text-align: center; padding: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched⁸</div>			Classification System	Classification Symbols	Int.Cl. 5	C07C											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; padding: 5px;">Category¹⁰</th> <th style="width: 70%; padding: 5px;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;"> CHEMICAL ABSTRACTS, vol. 112, no. 17, 23 April 1990, Columbus, Ohio, US; abstract no. 157828e, page 679 ; see abstract & JP,A,1 233 234 (MITSUBISHI KASEI CORP) 19 September 1989 <div style="text-align: center;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;"> US,A,4 375 571 (HART ET AL) 1 March 1983 see claims <div style="text-align: center;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;"> US,A,2 392 960 (C. W. WATSON) 15 January 1946 <div style="text-align: center;">---</div> </td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;"> DE,A,2 548 428 (BURMAH OIL TRADING) 13 May 1976 <div style="text-align: center;">---</div> <div style="text-align: right; padding-top: 10px;">-/--</div> </td> <td></td> </tr> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	CHEMICAL ABSTRACTS, vol. 112, no. 17, 23 April 1990, Columbus, Ohio, US; abstract no. 157828e, page 679 ; see abstract & JP,A,1 233 234 (MITSUBISHI KASEI CORP) 19 September 1989 <div style="text-align: center;">---</div>	1	X	US,A,4 375 571 (HART ET AL) 1 March 1983 see claims <div style="text-align: center;">---</div>	1,7	A	US,A,2 392 960 (C. W. WATSON) 15 January 1946 <div style="text-align: center;">---</div>		A	DE,A,2 548 428 (BURMAH OIL TRADING) 13 May 1976 <div style="text-align: center;">---</div> <div style="text-align: right; padding-top: 10px;">-/--</div>	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center; padding: 5px;">30 AUGUST 1993</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; padding: 5px;">- 7. 09. 93</div> </td> </tr> <tr> <td style="padding: 5px;"> International Searching Authority <div style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</div> </td> <td style="padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; padding: 5px;">J. VAN GEYT</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; padding: 5px;">30 AUGUST 1993</div>	Date of Mailing of this International Search Report <div style="text-align: center; padding: 5px;">- 7. 09. 93</div>	International Searching Authority <div style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center; padding: 5px;">J. VAN GEYT</div>											
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INTERNATIONAL SEARCH REPORT

International Application No

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>GB,A,552 115 (C. WEIZMANN) 13 March 1946</p> <p>-----</p>	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9306289
SA 76194

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4375571	01-03-83	None	
US-A-2392960		None	
DE-A-2548428	13-05-76	GB-A- 1488521	12-10-77
		JP-C- 1238085	31-10-84
		JP-A- 51068538	14-06-76
		JP-B- 59012089	21-03-84
GB-A-552115		None	

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